

A [HN(BH=NH)₂]²⁻ Dianion, Isoelectronic with a β-Diketimate

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Supporting Information

ABSTRACT: The 1:2 reaction of the Al(III) β-diketimate dihydride [{DMPnacnac}AlH₂] [DMPnacnac = {HC[C(Me)N(2,6-Me₂-C₆H₃)]₂] (**1**) with ammonia borane (NH₃BH₃) gives the new complex [{DMPnacnac}Al{NHBH₂NH}] (**3**), whose [HN(BHNH)₂]²⁻ dianion is isoelectronic with β-diketimate anions.

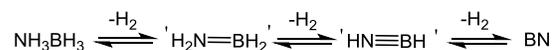
The dwindling supply of important elements combined with an ever-increasing population has led to a general shift of emphasis to more Earth-abundant elements in the chemistry world. In recent years there has been a major focus on the applications of both non-metallic and metallic main group species as stoichiometric and catalytic reagents for a range of molecular transformations, which are cheaper potential alternatives to transition metal analogues. One particular area of interests in this context has been dehydrocoupling reactions using molecular main group compounds, in which a homo- or hetero-atomic element-element bond is formed by the coupling of two element-H bonds, with the formal loss of H₂ (Scheme 1).¹



Scheme 1 Dehydrocoupling of two element-H bonds, with the release of dihydrogen.

A principle motivation in this area is the potential for the use of hydrogen-rich molecules as H₂-storage materials, most notably ammonia-borane (NH₃BH₃) containing 19.6 wt% H (Scheme 2).² One prerequisite for this is the development of catalytic processes for the fast release of H₂, which otherwise will not occur at or around room-temperature. A range of *s*- and *p*-block main group metal precatalysts has been shown to function as competent catalysts for H₂ release.³ More often than not, however, secondary and tertiary amine-boranes (R₂NHBH₃ or RNH₂BH₃) have been employed as models and very few studies have concerned NH₃BH₃ itself. Nonetheless, this work has shown that the mechanism of

dehydrocoupling has many features in common with transition metal catalyzed systems. In particular, dehydrogenation of amine boranes appears to involve metal hydrides as the active catalytic species.



Scheme 2 The concept of H₂ storage using NH₃BH₃.

Our investigations of the dehydrogenation of amine-boranes with Al(III) compounds have suggested that Al(III) dihydrides can be particularly active catalysts.^{4,5} However, steric factors can modify or severely limit these reactions. For example, Harder and coworkers have shown that although [{DIPPnacnac}AlH₂] (DIPP = 2,6-^tPr₂-C₆H₃) triggers stoichiometric release of H₂ with less sterically-demanding amine-boranes (giving mixtures of intractable products), only nucleophilic attack of H⁻ occurs in the case of more sterically encumbered DIPPNH₂BH₃ (to give BH₄⁻).⁶ Most interestingly, the stoichiometric reaction of [{DMPnacnac}AlH₂] (**1**) with NH₃BH₃ results in the unprecedented [HN(BHNH)₂]²⁻ dianion (**3**), which is isoelectronic with β-diketimate anions (Figure 1).

In the current paper, we show that even a small reduction in the steric domain of the nacnac ligand, from DIPPnacnac to DMPnacnac, can facilitate clean dehydrocoupling reactions with NH₃BH₃ or ^tBuNH₂BH₃.

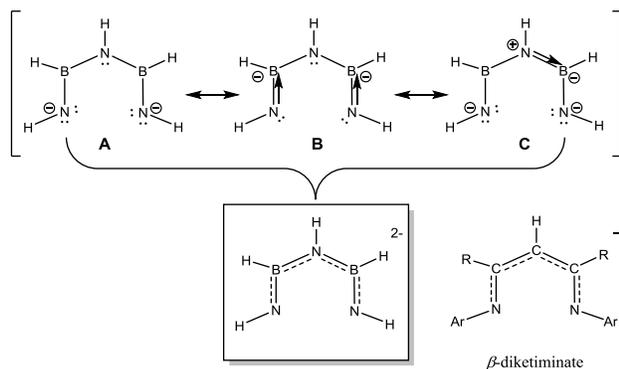


Figure 1 Valence-bond representation of the $[\text{HN}(\text{BH}_2\text{NH})_2]^{2-}$ dianion (top), and the relationship to β -diketiminate anions.

An *in situ* ^{11}B NMR spectroscopic study of the 2:1 reaction of NH_3BH_3 with **1** in THF shows the appearance of a BH_4^- -containing species at δ 41.8 ppm after 2h at room temperature (Figure 2b). After 72h this is joined by a second BH_4^- species at δ 37.7 ppm (Figure 2c). The latter species can be isolated as a crystalline solid from the reaction and was shown to be the mono-hydride $[\{\text{DMPnacnac}\}\text{AlH}(\text{BH}_4)]$ (**2**) (see Supporting Information). The formation of a borohydride is similar to the previously reported study of the reaction of $(\text{DIPP})\text{NH}_2\text{BH}_3$ with $[\{\text{DIPPnacnac}\}\text{AlH}_2]$ which gives rise to the *bis*- BH_4^- complex $[\{\text{DIPPnacnac}\}\text{Al}(\text{BH}_4)_2]$ by nucleophilic attack on $(\text{DIPP})\text{NH}_2\text{BH}_3$ by the Al-bound hydride. The structural features (Figure 3) and ^{11}B chemical shifts of **2** are very similar to those found in the previously reported *bis*-borohydride complex, both having the same κ^2 -coordination of the BH_4^- to Al.

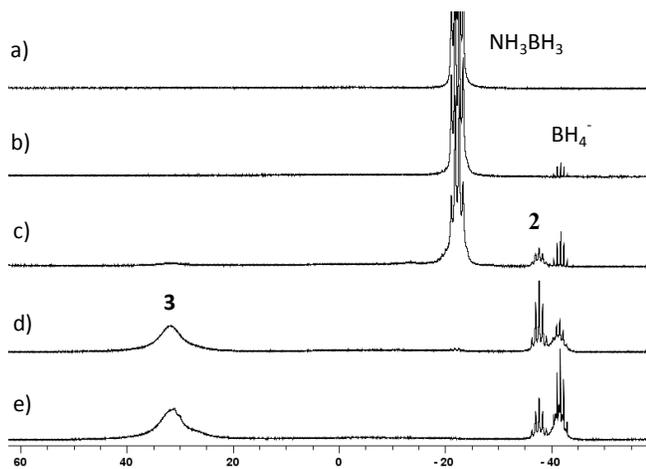


Figure 2 ^{11}B NMR spectroscopic study of the 2:1 reaction of NH_3BH_3 with **1** in THF after a) 5 mins, b) 2h, c) 72h, d) after additional 1h reflux, e) reflux after 24h.

Also apparent after *ca.* 72h at room temperature is a broad peak at δ 31.8 ppm (in the 2:1 reaction), consistent with an sp^2 hybridized boron atom, arising from the $[\text{NHBH}_2\text{NH}]^{2-}$ dianion (Figure 1). Further heating under reflux results in complete consumption of NH_3BH_3 and the formation of more of **3** (together with another BH_4^-

containing species, ^{11}B NMR δ 41.5) (Figure 2d and e). Extraction of the reaction products into *n*-hexane allowed the isolation of the crystalline complex $[\{\text{DMPnacnac}\}\text{Al}\{\text{NHBH}_2\text{NH}\}]$ (**3**) (in 16% yield, see Supporting Information). In addition to the ^{11}B NMR chemical shift, the formation of the unsaturated backbone of the $[\text{NHBH}_2\text{NH}]^{2-}$ dianion is supported by the presence of two broadly-separated N-H resonances at δ 3.88 and 2.81 (ratio 1:2, respectively) in the room-temperature ^1H NMR spectrum of crystalline **3** in C_6D_6 , along with a broad singlet (δ 4.69) for two magnetically-equivalent B-H protons (see Supporting Information, Figure S11).

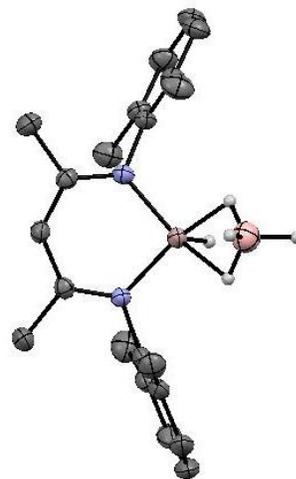


Figure 3 ORTEP view of the structure of **2**. Atoms are drawn at the 50% probability level. H-atoms, except the Al-H and BH_4^- atoms, have been removed for clarity. Selected bond lengths (\AA) and angles ($^\circ$): C(30)-N(1) 1.338(2), C(31)-N(2) 1.336(2), C(32)-C(31) 1.396(3), C(32)-C(30) 1.391(3), Al(1)-N(1) 1.8904(16), Al(1)-N(2) 1.8896(16), Al(1)-H(1) 1.51, Al(1)- μ -H(2,3) 1.74-1.79, B-H 1.08-1.17, N(1)-Al(1)-N(2) 96.15(7), N(1,2)-C(31,31)-C(32) range 119.57(16)-122.81(17), C(30)-C(32)-C(32) 127.37(17). Color key, brown (Al), blue (N), pink (B), grey (C).

The solid-state structure of **3** consists of a spirocyclic arrangement, in which a β -diketiminate $[\text{DMPnacnac}]^-$ monoanion and the $[\text{HN}(\text{BHNH})_2]^{2-}$ dianion chelate a distorted tetrahedral Al(III) cation (Figure 4a) (see Supporting Information). The ranges of the bond lengths and angles found in both of the independent (chemically-identical) molecules in the unit cell are given in the Figure caption, while average metric data are presented in Figure 4b. All of the H-atoms of the N-H and B-H groups were located in the difference map.

The six-membered AlN_3B_2 ring formed by the chelation of the $[\text{HN}(\text{BHNH})_2]^{2-}$ dianion to Al is almost perfectly planar (with the six atoms only deviating by *av.* 0.02 \AA). This and the range of B-N bond distances within N_3B_2 backbone, which are intermediate between the values expected for B-N single (*ca.* 1.51 \AA) and B=N double (*ca.* 1.31 \AA) bonds (B-N_{*a*} *av.* 1.39 and *av.* 1.43 \AA),¹⁰ suggests delocalization within the formally 6-electron π_p -system of the $[\text{HN}(\text{BHNH})_2]^{2-}$ dianion (see Figure 1). This view is

reinforced by the bond angles at the N and B atoms, which are all consistent with sp^2 hybridisation. In contrast to the planarity of the AlN_3B_2 , the C_3N_2Al unit formed by DMPnacnac-coordination of Al is envelope-shaped, with the Al atom being puckered out of the C_3N_2 plane by *ca.* 20.4° . This is probably the result of steric congestion around the Al atom.

To our knowledge the only example where the nacnac ligand framework has been substituted by isoelectronic B=N fragments is the so-called *baman* ligands reported by Chivers *et al.*¹¹ Here, replacement of one of the C=N units by a B=N has a dramatic effect on the bonding within the backbone, resulting in localized B=N and C=N bonds and in folding of the ligand upon metal coordination, as a consequence of a secondary N→M metal interaction. This situation is clearly very different to the delocalized situation found in the C_3N_2 backbone of nacnac ligands and in the $[HN(BHNH)_2]^{2-}$ dianion of **3**.

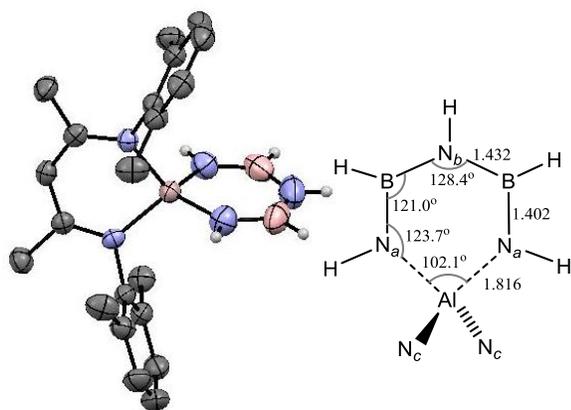


Figure 4 a) ORTEP view of the structure of **3**. Atoms are drawn at the 50% probability level. H-atoms, except those in the $[NHBH)_2NH]^{2-}$ dianion, have been removed for clarity. Selected bond lengths (Å) and angles ($^\circ$): within the $[HN(BHNH)_2]^{2-}$ dianion (ranges over the two independent molecules), Al- N_a 1.815(2)-1.817(2), B- N_a 1.398(4)-1.406(6), B- N_b 1.426(4)-1.438(4). N_a -Al- N_a 102.1(1), B- N_a -Al 123.7(2), N_b -B- N_a 120.5(2)-121.5(1), B- N_b -B 128.4(2), Al- N_c range 1.899(2), N_c -Al- N_c 85.51(8), Al(N_a) $_2$ B $_2$ (N_b) $_2$ within 0.01-0.03 of a plane. b) mean bond lengths and angles associated with the coordination of the $[HN(BHNH)_2]^{2-}$ dianion to the Al atom. Color key, brown (Al), blue (N), pink (B), grey (C).

The bonding within the $[HN(BHNH)_2]^{2-}$ dianion of **3** was investigated using DFT calculations using the B₃LYP functional¹² and the 6-31g++(d,p) basis set¹³ (see Supporting Information). The optimized structure of **3** is very similar to that observed in the solid state; the selected bond lengths and angles presented in Figure 5a can be compared to those in Figure 4b and match closely. While Wiberg Bond Index (WBI)¹⁴ and Natural Bond Order (NBO)¹⁵ analysis indicate that the N_b and the B atoms have sp^2 character, surprisingly, atoms N_a have approximate sp character. The NBO analysis also clearly indicates the presence of π_p bonding in the backbone of the dianion unit, with donation of electron density from the p -type lone pairs of N_a and N_b into the p -orbitals B-

atoms (perpendicular to the plane of the dianion). This results in an orbital occupancy of 0.38e in the B p -orbitals.

Figure 5b shows the principal bonding MOs involved in the π -system of the AlN_3B_2 ring system of **3**. HOMO-9 is an in-phase combination of all of the N and B p -orbitals of the dianion, while HOMO-2 involves a donor-acceptor interaction between the N_a and B atoms (with both MOs being nodal at Al). The HOMO corresponds to a π -donor interaction of the N_a p -orbitals with an Al p -orbital, in addition to the dominant σ -donor interaction of the other lone pair on N_a with the metal centre. Examination of the AlN_3B_2 ring unit using the Nucleus Independent Chemical Shifts (NICS) method indicates that this ring has weak aromatic character, with NICS(o) of -2.2 and NICS(1) of -1.4. For comparison, benzene has values of NICS(o) -8.3 and NICS(1) -10.3 at the same level of theory.

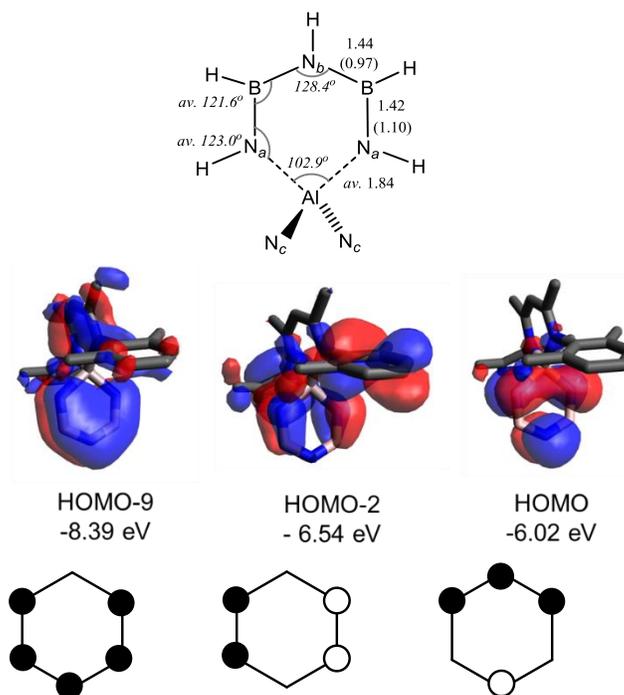


Figure 5 a) Bond lengths (Å), angles ($^\circ$) and (in parenthesis) bond orders for the optimized structure of **3**. b) π -MOs found in the AlN_3B_2 unit (shown schematically under each).

Finally, we investigated the potential roles that the borohydride **2** and the dianion complex **3** play in the substoichiometric (catalytic) dehydrocoupling of NH_3BH_3 . Using an excess of NH_3BH_3 (6 mol. eq.) with **1** gives borazine $[(NH)(BH)]_3$ (**4**) as the main product after 16h at reflux in THF (Supporting Information, Figure S3). Significantly, BH_4^- species are present throughout the course of the reaction, providing a first indication that aluminium borohydrides like **2** are the active intermediates. *In situ* ^{11}B NMR studies involving reactions of **1**, **2** and **3** with ammonia borane (6 eq.) in THF were undertaken. The overall conclusion drawn from these studies is that the mechanism of formation of borazine (**4**) is similar to that proposed for transition metal catalysed reactions,²³ with the previously observed borazane intermediates $[(BH_2)(NH_2)]_3$ ¹⁶ and

$[(N_3B_3H_{11})NH_2BH_3]$ ¹⁷ being observed for all of the reactions involving **1**, **2** and **3** (see Supporting information Figure S1 and Figure 6, below). Significantly, however, unlike the reactions involving **1** and **2**, no formation of BH_4^- is seen in the case of **3** at any stage. As shown in Figure 6, the reactions involving **1** and **2** produce a significant amount of **4** after 16h at 50°C. However, the amount of **4** formed in the case of **3** is little different from the control (ammonia borane alone). Furthermore, it is clear that borohydride **2** is a much more effective catalyst even than **1**, producing the greatest amount of **4** after this time. We therefore conclude that **3** is *not* involved significantly in the mechanism of formation of **4** and that the most likely catalyst is a borohydride (like **2**).

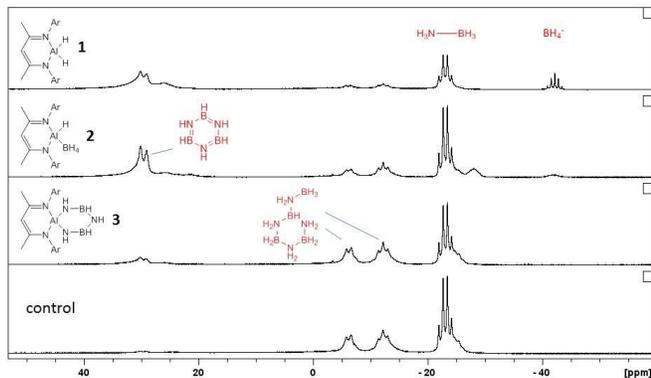


Figure 6 Comparison of the *in situ* ¹¹B NMR spectra of **1**, **2** and **3** + NH_3BH_3 (1:6 mol. eq.) in THF after 16h at 50°C.

Studies of the stoichiometric and sub-stoichiometric reactions of $tBuNH_2BH_3$ with **1** indicate a closely related dehydrocoupling mechanism to that seen with NH_3BH_3 (see Supporting Information Figures S4 and S5). However, unlike the NH_3BH_3 system, no tBu -substituted dianion analogue of **3** could be observed using any reaction stoichiometries. The 3:1 reaction of $tBuNH_2BH_3$ with **1** gives a mixture of tBu -substituted borazine [$tBuNBH_3$]₃ (**6**) and cyclic borazanes [$tBuHNBH_2$]_n after 16h reflux in toluene.

In conclusion, structural and theoretical studies of **3** show that the $[HN(BHNH)_2]^{2-}$ dianion has a similar delocalized bonding arrangement to isoelectronic nacnac relatives. We have also shown that Al(III) dihydrides supported by nacnac ligands can indeed dehydrocouple amine boranes if the steric bulk of the ligand is reduced. Thus, whereas no dehydrocoupling of NH_3BH_3 or $tBuNH_2BH_3$ was observed using $[(DIPPnacnac)AlH_2]$ ⁶, $[(DMPnacnac)AlH_2]$ is found to dehydrocouple both of these amine boranes (albeit at elevated temperature). Catalytic dehydrocoupling occurs by a similar mechanism to that found for transition metal catalyzed reactions, with aluminium BH_4^- complexes being the most likely catalytic species.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

NMR spectroscopic studies of stoichiometric and substoichiometric reactions of NH_3BH_3 and $tBuNH_2BH_3$, synthesis of **2** and **3**, X-ray data for **2** and **3**. Cif files for compounds **2** and **3** have been deposited with the Cambridge Crystallography Data Base (deposition numbers XXX and XXX, respectively).

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Notes

The author declares no competing financial interest.

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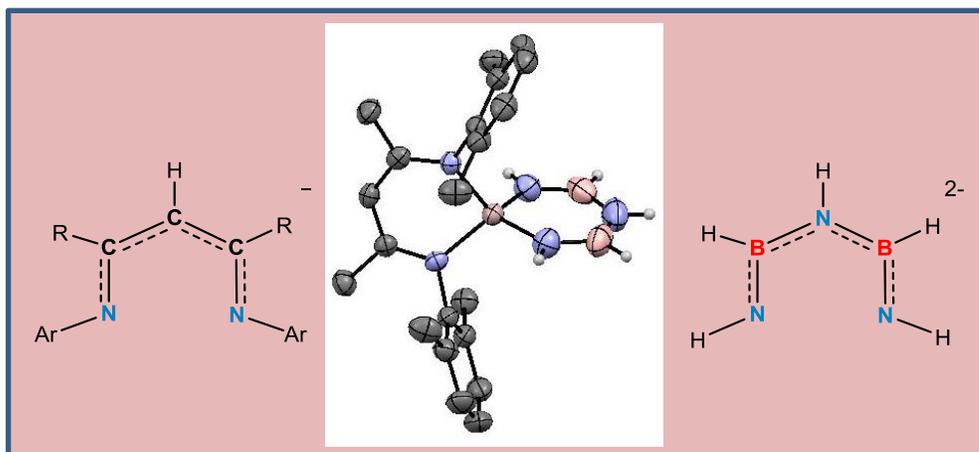
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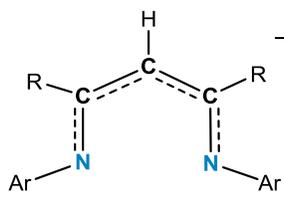
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